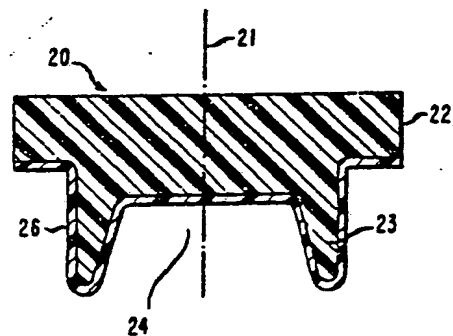
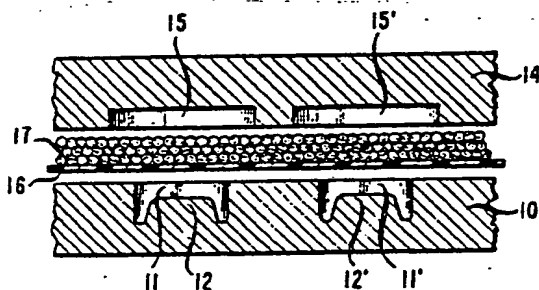




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification³ : B65D 51/00	A1	(11) International Publication Number: WO 84/ 03682 (43) International Publication Date: 27 September 1984 (27.09.84)
(21) International Application Number: PCT/EP84/00075 (22) International Filing Date: 14 March 1984 (14.03.84) (31) Priority Application Number: 476,075 (32) Priority Date: 17 March 1983 (17.03.83) (33) Priority Country: US (71) Applicant: SCHERING CORPORATION [US/US]; 2000 Galloping Hill Road, Kenilworth, NJ 07033 (US). (72) Inventor: KNAPP, Julius, Zigmund ; 22 Foxwood Drive, Somerset, NJ 08873 (US). (74) Agents: ANTONY, Fritz et al.; Technobiotic Ltd., P.O. Box 601, CH-6002 Lucerne (CH). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SE (European patent).		Published <i>With international search report.</i> <i>With amended claims.</i> <i>insb. Anspr. 1, 2.</i> = EP-A 0 140 910 = US 4 554 125 = US 4 635 807

(54) Title: IMPROVED STOPPER FOR STERILE FLUID CONTAINERS AND METHOD FOR MAKING SAME

**(57) Abstract**

A stopper (20, 44) for holding fluid (31, 43) in a container (30, 40) comprising: (a) a body of vulcanized elastomer having a convex surface (23, 45) and (b) a thin layer of thermoplastic (26) providing a surface for contacting the fluid (31, 43) and a part of the container (30, 40) and laminated without adhesive to a surface of the vulcanized elastomer (47). Also a method for making a stopper (20, 44) to hold fluid (31, 43) in a container (30, 40), said stopper (20, 44) having a thin layer of thermoplastic (26) laminated without adhesive to form a surface intended to contact the fluid (31, 43), comprising: (a) providing a first mold half (10) having a concavity (11, 11') and a second mold half (14) opposite the concavity (11, 11'), (b) disposing a sheet of thermoplastic (16) between the mold halves (10, 14) and vulcanizable elastomer (17) between the thermoplastic (16) and one of the mold halves (10 or 14), the thermoplastic (16) having an elongation of at least 450% and a crystalline melting point higher than the minimum vulcanizing temperature of the elastomer (17), (c) heating the mold halves (10, 14) to a temperature that is within the softening range and below the crystalline melting point of the thermoplastic (16) and above the minimum vulcanizing temperature of the elastomer (17), (d) pressing the heated mold halves (10, 14) toward each other with pressure sufficient to force elastomer (17) into the concavity (11, 11') while simultaneously forming thermoplastic (16) against the surface of one mold half (10 or 14), (e) holding the mold halves (10 and 14) in pressed position for a time sufficient to vulcanize the elastomer (17), and (f) removing the so-formed stopper (20, 44) from the mold.

IMPROVED STOPPER FOR STERILE FLUID CONTAINERS
AND METHOD FOR MAKING SAME

5 The present invention relates to stoppers for con-
tainers of injectable fluids. The vast majority of
such stoppers presently in use are made of elastomer,
such as natural rubber or butyl rubber. Rubber stoppers
have the advantage of a high degree of compliance, i.e.
flexibility or lack of stiffness, necessary to provide
a tight fit in the opening of a container. High
10 compliance is particularly important for stoppers of
mass-produced glass containers, since such containers
cannot be formed to close tolerance. Hence the stopper
must be sufficiently pliable to provide a tight steri-
lity barrier over a fairly wide range of opening sizes.

15 However, rubber stoppers have certain disadvantages.
One disadvantage is their tendency to cause particles
or flakes to enter the solution. Upon prolonged storage,
the rubber may react with the sterile fluid causing the
rubber to form particulates which are shed into the
20 fluid. Furthermore, it is difficult to completely clean
extraneous particules from rubber stoppers. Attempts
to thoroughly clean particles from the surface of rubber
abrade the surface. The abrasions can deteriorate into
particulates upon prolonged storage. Also, molded
25 rubber stoppers stick to the mold during the manufactu-
ring process unless a mold release agent is coated onto
the mold. However, if gaps occur in the mold release
coating small tears will form in the rubber when it is



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pulled away from the mold. These tears can also promote the formation of particulates upon prolonged storage.

Prior art attempts to alleviate these problems consisted of spray coating or bonding thermoplastic onto the surface of the stopper destined to contact the injectable solution. However, spray coating with a variety of surface finishes proved to be an inadequate solution because the spray-coated materials flaked away from the elastomeric substrate during long-term storage and produced particulate contamination. Any adhesive used to bond thermoplastic to the rubber can also contaminate the solution by migrating through the thermoplastic. This is a problem when the stopper is penetrated by the cannula of a hypodermic syringe in a multidose bottle of injectable fluid. Furthermore, if the laminated thermoplastic is thick, or if the thermoplastic chosen is not sufficiently flexible, the compliance of the stopper is reduced, potentially prejudicing sterility.

The present invention provides a stopper having a very thin layer of thermoplastic laminated to an elastomeric core without adhesive. The thermoplastic layer is manufactured relatively free of punctures, isolating the elastomer from the injectable solution. The stoppers are easy to clean and highly resistant to formation of particulates. The stopper of the present invention has substantially the same degree of compliance as the elastomer core and can be manufactured very easily and inexpensively. Furthermore, since the elastomer is well isolated from the solution by the thermoplastic barrier, it is possible to choose elastomers that would not be usable in direct contact with the solution. Hence, cheaper or more flexible elastomers may be chosen.

One aspect of the present invention comprises a method for making a stopper to hold fluid in a container, said



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stopper having a thin layer of thermoplastic laminated without adhesive to form a surface intended to contact the fluid, comprising:

- 5 (a) providing a first mold half having a concavity and a second mold half opposite the concavity,
- (b) disposing a thin sheet of thermoplastic between the mold halves and vulcanizable elastomer between the thermoplastic and one of the mold halves, the thermoplastic having an elongation of at least 450% and a
10 crystalline melting point higher than the minimum vulcanizing temperature of the elastomer,
- (c) heating the mold halves to a temperature that is within the softening range and below the crystalline melting point of the thermoplastic and above the minimum
15 vulcanizing temperature of the elastomer,
- (d) pressing the heated mold halves toward each other with pressure sufficient to force elastomer into the concavity while simultaneously forming thermoplastic against the surface of one mold half,
- 20 (e) holding the mold halves in pressed position for a time sufficient to vulcanize the elastomer, and
- (f) removing the so-formed stopper from the mold halves.

When the sheet of thermoplastic extends across more
25 than one mold portion, a plurality of stoppers will be produced, joined together by a web of thermoplastic at least (more probably by a web of thermoplastic and of elastomer); and under these circumstances the step (f) of removing the so-formed stopper from the mold halves
30 will include the step of cutting out the stopper. Alternatively, the stoppers can be molded without any interconnecting web of material. For example, the raw vulcanizable elastomer can be completely enclosed in an evacuated thermoplastic envelope, which can be molded into
35 a stopper. The raw elastomer can be in the form of



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granules or sheets of calendared unvulcanized material,
and the envelope can be evacuated before filling with the
elastomer or alternatively afterwards by puncturing a
filled envelope and evacuating the air. An advantage of
5 this embodiment is that it minimizes the presence of
air bubbles in the stopper without the need for carrying
out the molding operation under vacuum.

The concavity in the first mold half will of course
produce a convexity in the resulting stopper. Normally
10 the convexity will penetrate into the neck of the
container, so that the vulcanizable elastomer should be
disposed between the thermoplastic and the second mold
half. Alternatively, the method according to the inven-
tion can be used for example to produce a stopper for
15 an eyedropper with thermoplastic laminated on its
inside. For this purpose, the vulcanizable elastomer
must be between the thermoplastic and the first mold
half.

A second aspect of the invention comprises a stopper
20 for holding fluid in a container comprising:

(a) a body of vulcanized elastomer having a convex
surface, and

(b) a thin layer of thermoplastic providing a sur-
face for contacting the fluid and a part of the contai-
25 ner and laminated without adhesive to a surface of the
vulcanized elastomer.



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In a stopper prepared by the process of vulcanizing raw elastomer completely enclosed in an evacuated thermoplastic envelope, the thin layer of thermoplastic will of course enclose the vulcanized elastomer and provide
5 all the surface of the stopper and not only that surface for contacting the fluid and a part of the container.

In a stopper for a eyedropper, the thermoplastic will be laminated to the inner surface, that is to a concave surface of the vulcanized elastomer. When the
10 stopper is to be used for closing a vial, the thermoplastic will be laminated to the convex surface of the vulcanized elastomer.

For the better understanding of the invention, particularly preferred embodiments thereof will be described
15 with special reference to the accompanying drawings, wherein:

Figure 1 schematically illustrates apparatus with the mold halves open for forming stoppers in accordance with the invention prior to molding the stoppers;

20 Figure 2 illustrates the apparatus of Figure 1 with the mold halves closed;

Figure 3 is a cross sectional view of a stopper in accordance with the invention;

25 Figure 4 is a cross section of a bottle of injectable fluid stoppered with a stopper according to this invention; and

Figure 5 is a cross sectional view of a hypodermic syringe having a stopper in accordance with the invention.

30 Apparatus used for making stoppers in accordance with the invention is schematically illustrated in



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Figures 1 and 2. Ordinary molding apparatus for elastomeric materials, well-known in the art and currently used to make conventional rubber stoppers, may be used. A first mold half 10 having at least one concavity 11 is provided. It is preferred to provide a mold half having a multiplicity of concavities so that many stoppers may be molded simultaneously. Two concavities 11 and 11' are shown in Figures 1 and 2. When forming stoppers for use on vials of injectable fluid, it is preferred that there be convexities 12 and 12' within the concavities. Hence, concavities 11 and 11' terminate in annular depressions. This will provide a stopper having the shape shown in Figure 3.

A second mold half 14 is provided opposite concavities 11 and 11' in first mold half 10. Second mold half 14 may have circular concavities 15 and 15' opposite concavities 11 and 11' in first mold half 10.

A sheet of non-porous thermoplastic 16 is disposed between the mold halves. The thermoplastic has an elongation of at least about 450%, i.e., the thermoplastic is capable of stretching by at least about 4-1/2 times its original length without fracturing.

Vulcanizable elastomer 17 is disposed between sheet 16 of thermoplastic and second mold half 14. The elastomer may be in the form of granules as shown in Figure 1 or in the form of one or more sheets of calendered unvulcanized elastomer. Preferred vulcanizable elastomers are natural rubber and butyl rubber and blends thereof, and silicon rubber. The vulcanizable elastomer vulcanizes when its temperature is raised above a certain minimum vulcanizing temperature and maintained at that temperature for a sufficient period of time for vulcanization to occur. The elastomer and thermoplastic are chosen so that the crystalline



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melting point of the thermoplastic is higher than the minimum vulcanizing temperature of the elastomer. For example, typical polypropylene copolymers useful in practising the invention have crystalline melting
5 points of about 170°C . An elastomer useful with this material is butyl rubber having a minimum vulcanizable temperature of 140°C .

With mold halves 10 and 14 and thermoplastic sheet 16 and vulcanizable elastomer 17 disposed as shown in
10 Figure 1, the mold halves are heated to a temperature that is within the softening range and below the crystalline melting point of the thermoplastic and above the minimum vulcanizing temperature of the elastomer. If the materials described in the previous paragraph
15 are used, the mold halves would be heated to a temperature between 140 and 150°C ., more preferably about 145°C .

The mold halves are then pressed toward each other by means not shown with pressure sufficient to force
20 elastomer into concavities 11 and 11'. When this is done, the elastomer pushes the thermoplastic ahead of it into the concavities, stretching the thermoplastic and forming it against the surface of the concavities. Figure 2 shows the mold halves in pressed position. The
25 mold halves are held in the pressed position of Figure 2 for a time sufficient to vulcanize the elastomer. The mold halves are then opened and the stoppers are cut away from the web 18 of excess elastomer and thermoplastic to yield stoppers having the shape shown in
30 Figure 3. It has been found that the layer of thermoplastic makes an excellent release agent rendering removal of stoppers from the mold concavities very easy without generating small tears in the elastomer or thermoplastic.



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Preferably the space between the mold halves is evacuated prior to pressing the mold halves toward each other to minimize air bubbles in the finished product. Evacuation to an absolute pressure below 0.2 atmospheres is preferred. The vacuum may be attained by using a vacuum rubber press, well known in the art.

Figure 3 is a cross sectional view of a preferred shape of a stopper formed in accordance with the invention. Stopper 20 is circular when viewed from the top of Figure 2; hence rotation of the cross section shown in Figure 3 about axis 21 generates the stopper in three dimensions. Stopper 20 has an elastomeric flattened cylindrical top 22 with an annular protrusion 23 from top 22, i.e. a convex surface having a concavity 24. A layer of thermoplastic 26 is laminated without adhesive to the elastomer on the outside of annular protrusion 23 and on the inside of concavity 24. The exact mechanism by which the thin layer of thermoplastic is laminated to the elastomer without use of adhesive is not known. However, while not wishing to be bound by any particular theory, it is believed that at the vulcanizing temperature of the elastomer and within the softening range of the thermoplastic, the thermoplastic attains increased molecular mobility, without actually experiencing crystalline melting. This increased molecular mobility, combined with the molding pressure, is believed to generate an adhesive interaction between the elastomer and the thin sheet of thermoplastic.

The choice of thermoplastic is important. The thermoplastic must have an elongation of at least 450 percent and should laminate to the elastomer at the molding temperature and pressure without adhesive or special preparative treatment. Telfon and nylon are not acceptable because they fail to meet either of these criteria. Polyethylene homopolymer is acceptable, but

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not preferred because it cannot withstand the sterilization temperature of 121°C . to which it is desirable to subject the stopper prior to use. Polypropylene homopolymer is acceptable but not preferred because it can become brittle upon long-term storage or exposure to radiation. The preferred thermoplastic is a sheet of a propylene copolymer that is at most 0.009 cm. (0.0035 inch) thick, more preferably a copolymer formed by copolymerizing from 5 to 9 percent ethylene with from 91 to 95 percent propylene and having at least 500% elongation. Such copolymers are readily available on the market from Shell and Hercules.

The thickness of the thermoplastic sheet should be the minimum required to avoid rupture during the stretching that takes place in the forming step. Choosing thicker sheets reduces the degree of compliance, and hence the sealing ability, of the stopper. For stoppers shaped as shown in Figure 3 having outside diameter of cylinder 22 of about 13 mm., a thickness of 0.009 cm. (0.0035") is adequate and it is believed that even lower thicknesses would suffice. For larger stoppers, the thickness of the thermoplastic may be higher, but it is highly desirable that the thickness does not exceed 0.02 cm. (0.0075"). Of course, after forming, the thermoplastic laminated to the elastomer will be thinner than the initial thickness of the thermoplastic sheet.

Preferably, the thermoplastic polymer begins to soften at about 135 to 145°C . (more preferably 140°C .) and has a crystalline melting point of from about 150°C . to about 175°C . (more preferably about 165° to 170°C .). The elastomer chosen must have a minimum vulcanization temperature below the crystalline melting point of the thermoplastic. Finding a suitable vulcanizable elastomer is easy given the wide variety of choices available in



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natural and butyl rubber.

The temperature to which the mold halves are heated is not critical so long as the temperature is

(a) low enough to be below the crystalline melting point of the thermoplastic,

(b) high enough to be within the softening range of the thermoplastic, and

(c) high enough to be above the minimum vulcanization temperature of the elastomer.

10 For the materials described above, it is preferable to heat the mold halves to from about 140 to 148°C. The pressure applied to the mold halves is not critical so long as it is sufficient to mold the elastomer in the conventional manner, since the elastomer-molding pressure
15 is far more than that required to form the softened thermoplastic.

Sharp edges and corners in the mold design should be avoided, since they concentrate strain in the thermoplastic material. For best results, all corners should
20 have a minimum radius of 0.0025 cm. (0.0010").

Figure 4 illustrates the stopper of Figure 3 in place in the neck of a bottle of injectable fluid. Bottle 30 containing injectable fluid 31 has neck 32, wherein there is disposed stopper 20 of Figure 3. A thin
25 metal seal 33 is crimped over stopper 20 and flange 34 of bottle 30 to hold stopper 20 in place. A circular opening in metal seal 33 over thin portion 35 of stopper 20 is located above concavity 24 and permits penetration of thin portion 35 with the cannula of a hypodermic syringe, whereby injectable fluid can be with-
30 drawn from bottle 30 into the barrel of the syringe in a manner well-known in the art.

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Figure 5 illustrates a hypodermic syringe having a stopper formed in accordance with the invention. Syringe 40 has hollow barrel 41 and cannula (i.e., hollow needle) 42. Injectable fluid 43 is disposed within barrel 41. 5 Stopper 44 holds the fluid in the barrel. Surface 45, contacting the fluid, and the surface 46, contacting the bore of barrel 41, are covered with a thin sheet of thermoplastic laminated to the core of elastomer 47. The surface of the stopper outside the fluid has an en- 10 gagement means 48 such as an internal thread for engaging plunger rod 49. During storage, the pre-filled disposable syringe of Figure 5 would have an elastomeric needle guard (not shown) covering and stoppering cannula 42 in a manner well-known in the art.

15 A stopper such as that shown in Figure 5 can be produced by use of molds similar to those shown in Figs. 1 and 2 but shaped to produce the stopper shown in Fig. 5. The second mold half can have an externally threaded protrusion extending from its face. After molding, the 20 stopper can usually be simply pulled away from the threaded protrusion; alternatively it can be unscrewed by hand.

An eyedropper according to the invention can be molded by use of a first mold half having an appropriate concavity, a second mold half having an appropriate protrusion 25 extending into this concavity when the mold halves are pressed together, a sheet of thermoplastic between the mold halves, and vulcanizable elastomer between the thermoplastic and the first mold half. The resulting eyedropper stopper, in use, will contact the outside of the glass 30 eyedropper at the top; any liquid drawn into the eyedropper that inadvertently contacts the stopper will be prevented from contamination by the elastomer forming the inside surface of the stopper.



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For some applications, it may be desirable to laminate a sheet of thermoplastic to both sides of the stopper. This could be accomplished by disposing a second sheet of thermoplastic (not shown) between elastomer 17 and mold half 14 in Figure 1. The resulting stopper, having thermoplastic laminated to its top surface, would be easier to clean and to handle with automatic machinery.

It can be seen that stoppers made in accordance with the invention have several advantages over prior art rubber stoppers and over prior art rubber stoppers having a layer of thermoplastic adhering to a rubber core:

A. The high degree of compliance of rubber or other elastomer is not lost, because the layer of thermoplastic is very thin;

B. The thermoplastic is laminated to the elastomeric core without adhesive; hence the possibility of contaminating the solution with adhesive or adhesive component is eliminated;

C. It is very easy to clean the thermoplastic surface of particulates without causing tears in the elastomer;

D. The thermoplastic laminate is much less reactive with the solution than rubber, allowing for a much longer storage without contamination of the solution with particles of rubber;

E. During manufacture, the thermoplastic and elastomer are molded simultaneously, thereby eliminating the need to mold the thermoplastic first and then place the molded thermoplastic inserts into the mold for the elastomer as required by some prior art lamination methods;

F. Since the elastomer is isolated from the solu-



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tion, it is possible to choose elastomers that are not compatible with the solution, for example elastomers that are cheaper and/or more pliable.



CLAIMS:

1. A method for making a stopper to hold fluid in a container, said stopper having a thin layer of thermoplastic laminated without adhesive to form a surface
5 intended to contact the fluid, comprising:

(a) providing a first mold half having a concavity and a second mold half opposite the concavity,

(b) disposing a sheet of thermoplastic between the mold halves and vulcanizable elastomer between the
10 thermoplastic and one of the mold halves, the thermoplastic having an elongation of at least 450% and a crystalline melting point higher than the minimum vulcanizing temperature of the elastomer,

(c) heating the mold halves to a temperature that
15 is within the softening range and below the crystalline melting point of the thermoplastic and above the minimum vulcanizing temperature of the elastomer,

(d) pressing the heated mold halves toward each other with pressure sufficient to force elastomer into
20 the concavity while simultaneously forming thermoplastic against the surface of one mold half,

(e) holding the mold halves in pressed position for a time sufficient to vulcanize the elastomer, and

(f) removing the so-formed stopper from the mold
25 halves.

2. A method as claimed in claim 1 wherein step (f) includes the step of cutting out the stopper.

3. A method as claimed in claim 1 or claim 2 wherein the vulcanizable elastomer is disposed between the thermoplastic and the second mold half.
30

4. A method as claimed in claim 1 wherein in step (b) the raw vulcanizable elastomer is completely enclosed within an evacuated thermoplastic envelope.

SUBSTITUTE SHEET



5. A method as claimed in any of claims 1 to 4 wherein the thermoplastic is a polypropylene or a polypropylene copolymer, having an elongation of at least 500% and a crystalline melting point of about 150 to 175°C.

5 6. A method as claimed in any of claims 1 to 5 wherein the vulcanizable elastomer is natural rubber or butyl rubber.

10 7. A method as claimed in claim 6 wherein the mold halves are heated to a temperature of between 140 and 150°C.

8. A stopper for holding fluid in a container comprising:

(a) a body of vulcanized elastomer having a convex surface, and

15 (b) a thin layer of thermoplastic providing a surface for contacting the fluid and a part of the container and laminated without adhesive to a surface of the vulcanized elastomer.

20 9. A stopper as claimed in claim 8 wherein the vulcanized elastomer is natural rubber or butyl rubber.

10. A stopper as claimed in claim 8 or claim 9 wherein the thermoplastic is propylene or a propylene copolymer, e.g. a copolymer of propylene and ethylene.

25 11. A stopper as claimed in any of claims 8 to 10 adapted to seal containers of injectable fluid and comprising a flat top, an annular convex protrusion from the flat top and a concavity within the protrusion, wherein the layer of thermoplastic is laminated to the annular protrusion and concavity.

30 12. A stopper as claimed in any of claims 8 to 10 adapted to act as a plunger within a hypodermic syringe and further comprising engagement means on a side of the stopper not intended to contact the injectable fluid.



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13. A stopper as claimed in any of claims 8 to 11 wherein the vulcanized elastomer is completely enclosed in a thin layer of thermoplastic.

AMENDED CLAIMS

[received by the International Bureau on 27 August 1984 (27.08.84);
original claim 2 amended; original claims 1.3 to 13 unchanged]

1. A method for making a stopper to hold fluid in a container, said stopper having a thin layer of thermoplastic laminated without adhesive to form a surface intended to contact the fluid, comprising:
- 5 (a) providing a first mold half having a concavity and a second mold half opposite the concavity,
- (b) disposing a sheet of thermoplastic between the mold halves and vulcanizable elastomer between the thermoplastic and one of the mold halves, the thermoplastic having an elongation of at least 450% and a crystalline melting point higher than the minimum vulcanizing temperature of the elastomer,
- 10 (c) heating the mold halves to a temperature that is within the softening range and below the crystalline melting point of the thermoplastic and above the minimum vulcanizing temperature of the elastomer,
- 15 (d) pressing the heated mold halves toward each other with pressure sufficient to force elastomer into the concavity while simultaneously forming thermoplastic against the surface of one mold half,
- 20 (e) holding the mold halves in pressed position for a time sufficient to vulcanize the elastomer, and
- (f) removing the so-formed stopper from the mold halves.
- 25 2. A method as claimed in claim 1 wherein step (f) includes the step of cutting out the stopper.
3. A method as claimed in claim 1 or claim 2 wherein the vulcanizable elastomer is disposed between the thermoplastic and the second mold half.
- 30 4. A method as claimed in claim 1 wherein in step (b) the raw vulcanizable elastomer is completely enclosed within an evacuated thermoplastic envelope.

FIG. 1

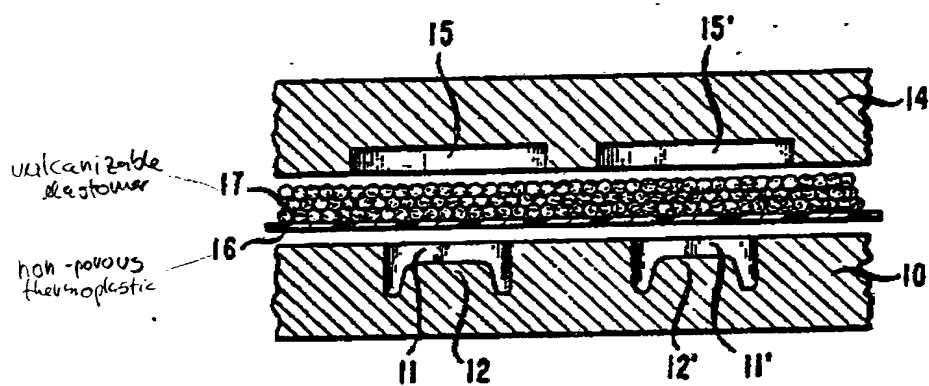


FIG. 2

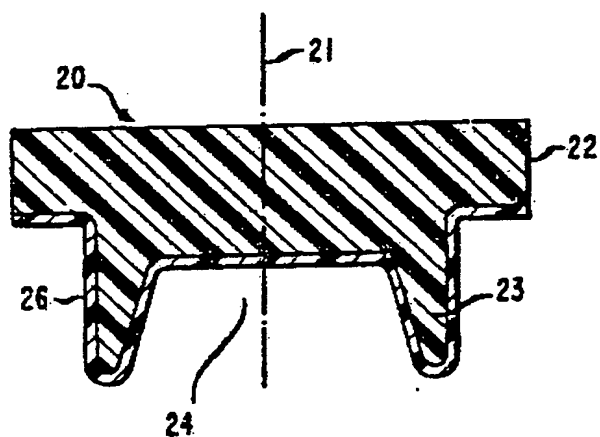
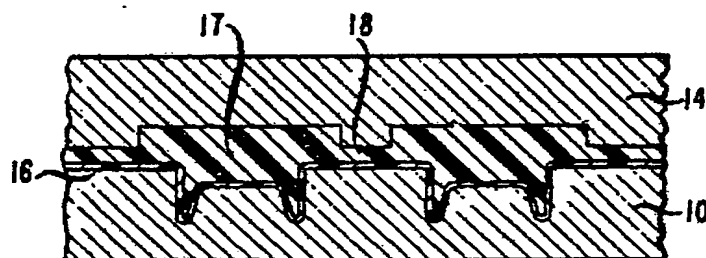


FIG. 3

2/2

FIG. 4

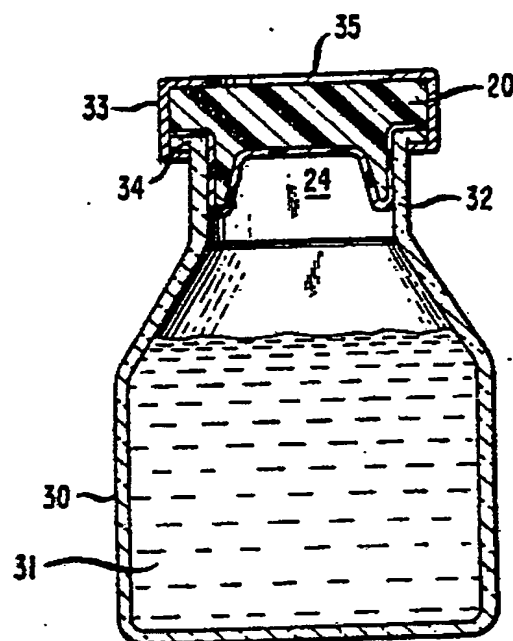
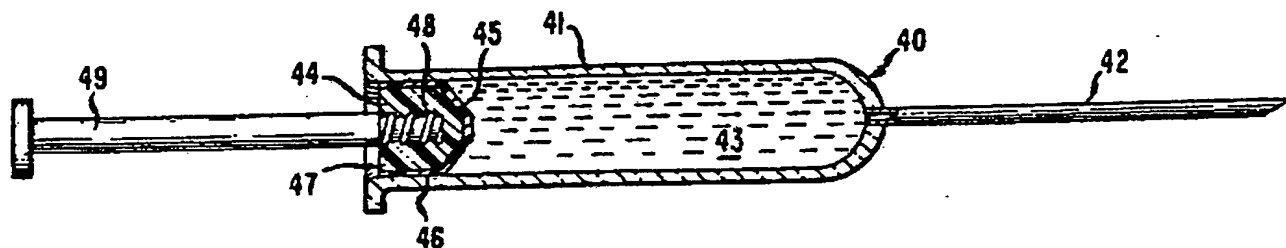


FIG. 5 *→ siehe S. 11, 2. Absatz*



INTERNATIONAL SEARCH REP RT

International Application No PCT/EP 84/00075

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC³: B 65 D 51/00

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System	Classification Symbols
IPC ³	B 65 D; B 29 H

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category *	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	FR, A, 1538462 (COLLOT) 6 September 1968 see the whole document	1,3,5,6,7,8, 9,10,11
Y	--	2,4,12,13
Y	FR, A, 1136064 (S.E.S.I.) 9 May 1957 see the whole document	2,4,12,13
A	US, A, 3547122 (RINSER) 15 December 1970 see column 2, line 30 - column 3, line 21; figure 1	12
A	FR, A, 2106567 (TAKEDA) 5 May 1972 see page 7, line 21 - page 8, line 29; page 11, line 19 - page 12, line 35; figures	1,3,6,8,9,11
A	GB, A, 1187350 (PHARMA-GUMMI WIMMER WEST) 8 April 1970 see page 3, lines 66-87; page 4, lines 48-104; figures	1,3,6,8,9

* Special categories of cited documents: ¹⁸

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"P" document published prior to the international filing date but
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"T" later document published after the international filing date
or priority date and not in conflict with the application but
cited to understand the principle or theory underlying the
invention

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cannot be considered novel or cannot be considered to
involve an inventive step

"Y" document of particular relevance; the claimed invention
cannot be considered to involve an inventive step when the
document is combined with one or more other such docu-
ments, such combination being obvious to a person skilled
in the art

"Z" document member of the same patent family

IV. CERTIFICATE

Date of the Actual Completion of the International Search ¹

29th May 1984

Date of Mailing of this International Search Report ²

04 JUL. 1984

International Searching Authority ³

EUROPEAN PATENT OFFICE

Signature of Authorized Officer ²⁰

G.L.M. Kruyenbergh

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/EP 84/00075 (SA 6745)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 22/06/84

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 1538462		None	
FR-A- 1136064		None	
US-A- 3547122	15/12/70	GB-A- 1172348 GB-A- 1168188	26/11/69 22/10/69
FR-A- 2106567	05/05/72	NL-A- 7112762 DE-A- 2146421 CH-A- 531347 GB-A- 1342975 US-A- 3760969	20/03/72 13/04/72 15/12/72 10/01/74 25/09/73
GB-A- 1187350	08/04/70	US-A- 3552591 CH-A- 487775 FR-A- 1598220 BE-A- 724540 SE-B- 353018	05/01/71 31/03/70 06/07/70 02/05/69 22/01/73